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A Growing-Drop Technique for Measuring
Dynamic Interfacial Tension

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ABSTRACT

A novel, growing-drop technique is described for measuring dynamic interfacial tension due to sorption of surface-active solutes. The proposed method relates the instantaneous pressure and size of expanding liquid drops to interfacial tension and is useful for measuring both liquid/gas and liquid/liquid tensions over a wide range of time scales, currently from 10 ms to several hours. Growing-drop measurements on surfactant-free water/air and water/octanol interfaces yield constant tensions equal to their known literature values.

For surfactant-laden, liquid drops, the growing-drop technique captures the actual transient tension evolution of a single interface, rather than interval times as with the classic maximum-drop-pressure and drop-volume tension measurements. Dynamic tensions measured for 0.25 mM aqueous 1-decanol solution/air and 0.02 kg/m³ aqueous Triton X-100 solution/dodecane interfaces show nonmonotonic behavior, indicating slow surfactant transport relative to the imposed rates of interfacial dilatation. The dynamic tension of a purified and fresh 6 mM aqueous sodium dodecyl sulfate (SDS) solution/air interface shows only a monotonic decrease, indicating rapid surfactant transport relative to the imposed rates of dilatation. Conversely, an aged SDS solution, naturally containing trace dodecanol impurities, exhibits dynamic tensions which reflect a superposition of the rapidly equilibrating SDS and the slowly adsorbing dodecanol.

INTRODUCTION

When a surfactant-laden fluid-fluid interface is stretched or contracted, surfactant exchanges with the bulk phases and transports along the interface to re-establish equilibrium. Convective-diffusion in both the bulk and surface phases, sorption kinetics, and molecular rearrangement at the interface all play roles in the overall kinetics. Thus, size and structure of the adsorbing molecules is an underlying factor that governs which transport resistance is controlling. For example, short (less than 14 carbons) straight-chain nonionic surfactants with small polar head groups (alcohols, phosphine oxides, carboxylic acids) display fast interfacial kinetics compared to diffusion to a liquid/gas surface (1-3). Conversely, specific proteins adsorbing at the aqueous/air interface undergo interfacial molecular rearrangements that are quite slow compared to times for bulk diffusion (4). Clearly, knowledge of surface adsorption and reaction kinetics first requires information about any convective-diffusion rates.

One method for studying surfactant adsorption/desorption kinetics at deformable interfaces is to measure the dynamic interfacial tension (5). Upon disturbing the interface, the tension is monitored as a function of time to reflect surfactant accumulation. Elucidation of sorption kinetics from such experiments demands that the surface be disturbed such that bulk convection and/or transport along the interface are either nonexistent or readily quantified. Further, the dynamic tension measurement should cover a wide range of experimental times and be applicable to liquid/liquid interfaces as well as to liquid/gas interfaces.

Current dynamic tension techniques suffer from limited time ranges, either short (oscillating or contracting jets (6-9)) or long (dynamic Wilhelmy plate or Du Nouy ring (3); dynamic pendant or sessile drops (1, 10, 11)), and from nontrivial hydrodynamics and/or hydrodynamics that are strongly influenced by surfactant transport (maximum bubble pressure (12-14); dynamic drop volume (2,

15); oscillating and contracting jets; inclined plane (16)). Certain methods obtain only a "snapshot" of tension taken at one instant during a transient process (dynamic drop volume; maximum bubble pressure). Some of the transient tension measurements apply only to liquid/gas interfaces (Wilhelmy plate; Du Nouy ring; maximum bubble pressure; inclined plane), while others probe primarily small deviations from equilibrium (oscillating bubble (17, 18); longitudinal waves (19, 20)).

We desire a more general technique for determining dynamic interfacial tension. Ideally this technique should span a large time range from ms, pertinent for short chain surfactants (e.g., sodium dodecyl sulfate (21)), to h, such as for surfactant mixtures containing dilute impurities (22) or for slowly unfolding proteins (4). Further, the desired technique should apply to both liquid/gas and liquid/liquid interfaces and to fluids exhibiting small density contrast, and the technique should be capable of monitoring the transient tension in real time. Most importantly, the interfacial shape disturbance must follow well-defined kinematics so that any convection and/or transport along the deformed interface can be quantitatively accounted for in data interpretation. To that end we propose a growing-drop apparatus.

Picture a small, more dense liquid drop growing in the direction of gravity from a capillary tip into a second, less dense fluid. As the drop expands, its pressure and curvature are monitored to detect the dynamic interfacial tension. The growing-drop geometry is identical to that used in the dropping mercury electrode (DME), which is known to approximate purely radial flow in the suspended droplet (23). It is the allure of radial growth along with applicability to a wide range of fluids and time scales that gives the growing-drop technique powerful appeal.

THE GROWING-DROP TECHNIQUE

Figure 1 shows schematically a liquid drop growing at a capillary tip of radius R_t . Two measures of drop size are shown, R_1 , the horizontal drop radius at the equator, and z_e , the vertical distance from the drop apex to the equator. The relative roles of interfacial tension and gravity in determining the drop shape are quantified by the drop Bond number,

$$Bo \equiv \frac{|\Delta\rho|gR_1^2}{\sigma}, \quad [1]$$

where $\Delta\rho$ is the density difference between the inner and outer fluids, $\rho_1 - \rho_2$, g is the acceleration due to gravity, and σ is the interfacial tension. In the limit of zero Bo , tension forces dominate, and the growing drop is spherical with $R_1 = z_e = R$, where R is the radius of an equivalent constant curvature drop.

A normal stress balance across a stretching spherical interface (24) suggests a means of monitoring the droplet interfacial tension as it grows:

$$\Delta P = \frac{2\sigma}{R} + \frac{4\kappa}{R^2} \frac{dR}{dt} + \frac{4\Delta\mu}{R} \frac{dR}{dt}. \quad [2]$$

In this equation, ΔP is the pressure difference between the inside and outside of the drop, $P_1 - P_2$, dR/dt is the radial velocity of the drop surface, $\Delta\mu$ is the difference between the inner and outer fluid viscosities, $\mu_1 - \mu_2$, and κ is the interfacial dilatational viscosity. As long as $(\Delta\mu dR/dt)/\sigma \ll 1$, which is the case in our experiments (i.e. $(\Delta\mu dR/dt)/\sigma \approx 10^{-5}$), the bulk viscous stress term is negligible in comparison with the interfacial tension term. The magnitude of the surface viscosity term is more difficult to assess, since surface dilatational viscosities have not been extensively measured. Recently Kao et al (25) show that for short chain surfactants, such as SDS and octanoic acid at the water/air interface, the surface dilatational viscosity is of the order of $10^{-5} \text{ mN}\cdot\text{s}\cdot\text{cm}^{-1}$. It thus appears that for typical surfactants the surface viscosity term is also

negligible at the rates of expansion ($(dR/dt)/R \approx 1s^{-1}$) used in our growing-drop experiments. By neglecting these two viscous terms, Eq [2] reduces to the familiar Young-Laplace relationship:

$$\Delta P(t) = \frac{2\sigma(t)}{R(t)}, \quad [3]$$

which shows that by simultaneously measuring the pressure change across the drop interface and the drop radius as a function of time, t , the dynamic interfacial tension, $\sigma(t)$, can be monitored throughout drop growth.

The configuration of a drop growing at a capillary tip is identical to that used in the dynamic drop-volume technique (2, 15), which relates the volume of a drop detaching from a capillary tip to the interfacial tension at the instant of detachment. Like the drop-volume technique, the growing-drop technique is applicable to both liquid/gas and liquid/liquid interfaces. However, since the drop need not detach from the tip for a measurement to be obtained, the growing-drop technique remains useful even in the limit of vanishing density difference between the inner and outer fluids. Further, the growing-drop method continuously monitors the tension throughout drop lifetime, and thus reveals a complete history of dynamic interfacial events. This is in direct contrast with the drop-volume technique, which obtains only a single measure of tension as the drop detaches.

The hydrodynamics of a drop growing from a capillary are in general very complex, but under specific experimental conditions pure radial growth occurs. Humphrey and Hummel (26) used flow visualization techniques to study the hydrodynamics in growing drops of surfactant-free fluids. They define a drop circulation number which is the product of modified Weber and Reynolds numbers. When operating at circulation numbers less than unity, they find

radial flow in the drops. At higher circulation numbers there is a transition to jetting flow in the drops.

The presence of surfactants at the interface further reduces the amount of internal circulation in the drops. This is commonly observed with the dropping mercury electrode, where surfactants are sometimes added to the solution to suppress circulation in the mercury drop and extend the range of conditions over which pure radial flow occurs (27). The governing principle is that small gradients in tension along the interface lead to shear stresses which rigidify the surface (23).

Only very small tension changes over a drop surface are necessary to eliminate tangential interfacial motion. As a crude approximation to the growing drop, consider an isolated sphere in a liquid of viscosity μ , traveling at a velocity U . The tension gradient needed to rigidify totally the spherical interface is given by (28):

$$\frac{d\sigma}{d\theta} = -\mu U \sin \theta, \quad [4]$$

where θ is the azimuthal angle, and μ is the viscosity of the outer fluid. If we approximate U as the average velocity of fluid emerging from the tip and μ as the inner fluid viscosity, μ_1 , and we substitute typical experimental values, Eq. [4] reveals that total rigidification of the interface requires occurs with only a 0.01 mN/m tension gradient from front to back of the drop.

These arguments suggest that, for a well-defined range of experimental conditions, the fluid flow in a growing drop is nearly radial. Under these conditions the convective-diffusion equation can be solved to account quantitatively for both diffusive and convective solute transport within the bulk fluids, in a manner similar to the Ilkovic analysis of the DME (29). Establishment of radial flow is a major advantage of the growing-drop technique, for it permits rigorous modeling of the transport mechanisms at an expanding interface.

EXPERIMENT

Procedures

Figure 2 illustrates the growing-drop apparatus. It is similar to that of Passerone et al (30) for studying equilibrium tensions in a micro-gravity environment. An ISCO Model 100D syringe pump supplies liquid, at flow rates down to $0.1 \text{ mm}^3/\text{min}$, through stainless steel tubing to a stainless steel capillary tip. Pump pulsation is eliminated by an ISCO 100 psi back pressure regulator, located in the liquid line. An Endevco Model 8510B-2 piezoresistive differential pressure transducer (range 0-2 psi) gages the liquid pressure in the growing drop. Before use the supplied screen protecting the sensor face is removed to assure complete liquid contact. An Endevco Model 4428 conditioning unit amplifies the signal, and a Remote Measurement Systems Model ADC-1 A/D converter digitizes and transmits the signal to an Apple Macintosh IIci computer at sampling rates up to 50 Hz. A standard video camera and recorder monitor the drop radius. The capillary tip rests in a Plexiglas measurement cell, approximately 6 cm x 4 cm wide and 6 cm tall, which is jacketed for temperature control. The transducer is located just outside the cell and is referenced to atmospheric pressure. Accordingly, the cell is vented to maintain the vapor inside at atmospheric pressure.

Pressure resolution, which is the main factor controlling measurement precision, is limited by noise in the pressure signal. Drop vibration is the primary source of this noise. Weighting the cell lid directly above the tip reduces pressure fluctuations to an amplitude of approximately 1 Pascal. For typical drop sizes of 1 mm, pressure noise leads to a maximum scatter of around 1 mN/m in the tension values.

Modified Luer-Lok syringe needles of sizes ranging from 0.30 to 0.51 mm OD serve as the drop-forming capillary tips. The capillaries are cut to approximately 3 mm in length and carefully sanded to a perpendicular edge. Wetting behavior of the tips has a critical impact on the growing-drop measurement. Figure 3 illustrates the droplet configurations which result from various capillary-tip wettabilities. When the tip is preferentially wet by the outer fluid, as in Fig. 3a, the three-phase contact line is pinned at the inner edge of the tip face. If the inner fluid strongly wets the tip, however, we find that the three-phase contact line moves up the tip and the drop "climbs" the outside wall of the capillary per Fig. 3b. Further, when the inner fluid only partially wets the tip, the drop initially grows from the inner radius of the capillary, and as the drop expands the contact line slides across the tip face to pin at the outer edge. The resulting contact-line motion, illustrated in Fig. 3c, is abrupt and nonuniform. Both phenomena obviate the dynamic tension measurement. Thus, we prefer that the inner drop-forming liquid not wet the capillary tip.

For liquid/liquid systems there is no difficulty in choosing the nonwetting phase as the inner drop-producing fluid. For liquid/gas systems, however, the liquid phase which must form the drops usually preferentially wets the capillary tip. With strongly wetting liquids against air in our stainless-steel capillaries, such as alkanes, alcohols, aromatics, and aqueous surfactant solutions above the critical micelle concentration (CMC), we have been unsuccessful in overcoming drop climbing. For less preferentially wetting liquid drops grown into air, such as aqueous surfactant solutions below the CMC, roughening the tip face with a 600 grain abrasive permits consistent drop growth from the outer tip radius (see Fig. 3d).

Figure 4 shows an expanded view of the measurement cell. The transducer monitors a pressure, ΔP_m , which is related to the dynamic interfacial tension by

$$\Delta P_m = \frac{2\sigma}{R} + \Delta P_v + \rho_1 g h_1 + \rho_2 g h_2, \quad [5]$$

where ΔP_v is the pressure drop due to viscous losses between the transducer and drop, h_1 is the vertical distance between the transducer and tip faces, and h_2 is the level of the outer fluid-gas interface relative to the tip face in liquid/liquid measurements ($\rho_2 \approx 0$ for liquid/gas systems). Equation [5] demands that the tip capillary Reynolds number and the Bond number are low enough that the pressure within the drop is uniform and the drop radius, R , is independent of surface position.

The growing-drop experiment is performed at Reynolds numbers ($Re \equiv \rho_1 U D_t^2 / \mu_1$, where D_t is the tip inner diameter, and U is the average velocity of the fluid in the tip) much less than unity. At such low Re the pressure drop due to laminar flow through the tip can readily be calculated using the Hagen-Poiseuille equation. However, by slightly immersing the end of the tip into the bulk liquid that forms the drop, the measured pressure drop is observed to exceed the calculated Hagen-Poiseuille pressure drop by approximately 50%. The source of the additional pressure drop is the contraction in the fitting leading to the tip. Accordingly, contraction losses were measured independently by removing the tip from an identical fitting containing an orifice of diameter equal to the inner tip diameter. By adding the measured contraction losses to the Hagen-Poiseuille capillary losses we match the measured total pressure loss, ΔP_v , exactly (29).

Before conducting an experiment, all components which come in contact with the liquid(s) are cleaned with isopropyl alcohol (Fisher, spectroscopic grade) and rinsed with copious amounts of distilled, deionized water. The system is then

rinsed several times with the surfactant solution to be studied. For liquid/liquid measurements the cell is first filled halfway with the drop solution, and the less dense outer liquid is added until the tip is slightly immersed. For liquid/gas measurements the cell is partially filled with the drop solution. The cell is then sealed and connected to the vented reservoir of saturating solution.

A constant flow rate is established, and transient pressure and radius data are accumulated for several consecutive drops. After each measurement series, the liquid level in the cell is raised by injecting droplet liquid from a separate glass syringe into the cell. When the end of the tip is slightly immersed in this denser liquid, the "zero" ($\sigma=0$) pressure drop, ΔP_m^0 , is measured:

$$\Delta P_m^0 = \Delta P_v + \rho_1 g h_1^0 + \rho_2 g h_2^0, \quad [6]$$

where h_1^0 is the height of the dense liquid meniscus relative to the transducer face, and h_2^0 is the depth of the lighter phase. By averaging over 500 individual pressure readings, the "zero" pressure is measured to within 0.1 Pa. Subtracting Eq. [6] from Eq. [5]:

$$\Delta P_m = \frac{2\sigma}{R} + \Delta P_m^0 + \rho_1 g (h_1 - h_1^0) + \rho_2 g (h_2 - h_2^0), \quad [7]$$

shows that an accurate "zero" pressure measurement eliminates the need for extensive pre-experiment calibration of viscous losses for different tips. More importantly, the measurement of the relative positions of the transducer and tip faces, which is difficult to assess because the transducer face is recessed in the casing, is replaced by the measurement of the hydrostatic heads $(h_1 - h_1^0)$ and $(h_2 - h_2^0)$. These are easily determined to ± 0.1 mm using a Wild Model KM 247 cathetometer.

Typical raw data for water drops growing in air at ambient temperature are shown in Fig. 5. The pressure signal increases rapidly to a distinctive

maximum after drop detachment, which corresponds to a minimum drop radius equal to the tip radius. This well-defined point is used to calculate a surface tension that is directly analogous to the maximum-bubble-pressure measurement. As the drop grows from a hemisphere, the pressure inside the drop falls. From the pressure and radius data, the surface tension is calculated between the time the drop is hemispherical and the time the drop detaches via Eq. [7]. At drop detachment the drop-volume technique provides another independent measurement of the surface tension: $\sigma = \Delta p g V_d / 2\pi R_t f$, where f is a correction factor and is a unique function of the ratio of the tip radius and the drop volume, V_d , to the 1/3 power. Correction factors measured specifically for small tip sizes are used (31). The drop-volume detachment tension is compared to the final tension obtained from the growing-drop pressure measurement.

Because accurate measurement of drop sizes from video images is painstaking without digitizing the signal, an independent method of establishing the transient drop radius was developed. The radius, R , of a spherical section at the end of a tip of known radius, R_t , can be expressed in terms of the distance, z_t , between the drop apex and tip: $R = R_t^2 / 2z_t + z_t/2$. The volume of this drop is given by: $V = 2\pi z_t R^2$. Finally, at constant volumetric flow, Q , the drop volume obeys the linear relation: $V(t) = V_0 + Qt$, where t is the time relative to that for the hemispherical drop of volume V_0 . Combining these equations gives a third order polynomial equation that can be solved analytically for the radius R needed in Eq. [7] as a function of time:

$$\frac{2R}{R_t} = (\alpha_+ - \alpha_-) + (\alpha_+ - \alpha_-)^{-1} \quad [8a]$$

where

$$\alpha_{\pm} = \left\{ \left[R_t^6 - \frac{9}{\pi^2} (V_o + Qt)^2 \right]^{\frac{1}{2}} \pm \left[\frac{6}{\pi} (V_o + Qt) \right] \right\}^{\frac{1}{3}} / R_t . \quad [8b]$$

In order for Eq. [8] to apply to the growing drop experiment, two conditions must be met. First, the volumetric flow rate into the drop must be carefully held constant during drop growth, and second, the drop must be small enough to maintain sphericity.

Compression of any unwanted gas bubbles in the liquid lines can lead to nonconstant flow during the early stages of drop growth (32). Figure 6 shows pressure traces for water drops growing in air, obtained by purposely attaching a syringe containing varying volumes of gas to the liquid line just upstream from the transducer. These experimental traces are compared to the pressure calculated from Eqs. [7] and [8] and 72.5 mN/m for the tension of water. As the gas volume in the line increases, the time required for the pressure to reach a maximum and the rate at which the pressure falls after the maximum increase. In the limit of large gas volume, the pressure change mimics that seen in maximum bubble pressure experiments (13). At the highest added gas volume, drop growth is further complicated by recession of the remnant drop interface into the capillary tip immediately following detachment. The resulting decrease in pre-hemispherical radius leads to the high value of pressure at early times, which is seen in the pressure trace for 6 cm³ added gas.

The dramatic effect of gas volume on the growing-drop pressure evolution is explained by considering the effect that pressure changes have on the compressible gas. At early times after detachment the drop radius decreases from close to infinity to that of the inscribed hemisphere of the capillary tip. The corresponding pressure increase compresses any gas in the system. A portion of the flowing liquid fills the volume vacated by gas resulting in a decrease in the

actual liquid flow rate into the drop and a slow pressure increase. When the drop grows beyond hemispherical, the pressure in the drop decreases and the compressed gas expands, causing a rapid initial increase in drop size. Thus, in the presence of undesired gas, the liquid flow rate into the drop is not constant in spite of constant piston displacement, and the time dependence of liquid flow is a function of both the ratio of maximum to minimum pressure and the ratio of spurious gas volume to drop volume. Constant growth of a drop can be maintained only when no gas and/or mechanical compressibility is present.

Accordingly, we take great care to remove gas bubbles from the growing-drop apparatus. The pump and liquid lines are filled with the pure liquid of interest, and the pressure evolution for the pure liquid drop (i.e. $s = \text{constant}$) growing into air is measured and compared to the calculated gas-free case. Even when all bubbles have been removed from the lines, any elasticity of the transducer face, pump seal or fittings leads to slight discrepancies between the measured and calculated pressure profiles during the pre-hemisphere growth period. When this discrepancy occurs only over the first 1% of the drop lifetime for the pure fluid, the pump is filled and the liquid in the lines is displaced with surfactant solution without introducing gas into the system. If the discrepancy occurs over longer times, the liquid lines are drained and refilled until the constant-flow criterion is met.

The second restriction on Eq. [8] is drop sphericity, which demands low Bond numbers. The validity of the spherical-drop assumption can be examined by considering the two measures of drop size graphed in Fig. 5. Over the first third of the drop lifetime, the measured vertical distance from the tip to the drop equator, $z_t - z_e$, and the horizontal drop size at the equator, R_1 , follow the low Bond number approximation in Eq. [8] exactly. At later times during drop growth, $z_t - z_e$ becomes significantly larger than R_1 , indicating that the drop no

longer remains spherical. To interpret growing-drop data over the last two thirds of drop growth, it is necessary to correct for this drop elongation.

For an elongated drop the normal stress balance of Eq. [3] should be rewritten as

$$\Delta P(z) = \sigma \left(\frac{1}{R_1(z)} + \frac{1}{R_2(z)} \right) = \frac{2\sigma}{R_m(z)}, \quad [9]$$

where R_1 and R_2 are the local principal radii of curvature and R_m is the corresponding local mean radius of curvature. By defining $z = 0$ as the location of the drop apex, the pressure drop across the interface is also described by,

$$\Delta P(z) = \frac{2\sigma}{R_m(0)} - \Delta \rho g z. \quad [10]$$

In the static case rigorous solutions to Eqs. [9] and [10] are available (33). These solutions give complete drop profiles and drop volumes for pendant drops as a function of the Bond number and establish a relationship between the constant curvature radius, R , calculated by Eq. [8], and the mean radius of curvature at various locations of an elongated drop of the same volume. Figure 7 shows a plot of the ratio of $R_m(z)/R$ as a function of Bond number for three values of z . For $Bo < 0.01$ the mean radius of curvature is everywhere equal to R . For $Bo > 0.01$ the drop elongates, and R_m varies with position. The mean radii at the drop apex and near the tip deviate significantly from the spherical approximation. However, even for the largest Bond number used in our experiments, $Bo \approx 0.35$, the mean radius at the equator deviates by less than 5% from the spherical radius calculated by Eq. [8]. We accept this error and adopt Eq. [8] to calculate the mean radius of the drop at the equator. More precise image analysis of the growing drop would alleviate this approximation.

Equation [7] also assumes drop sphericity and thus makes no correction for hydrostatic pressure differences within the drop. When the drops elongate this omission must be corrected. Equation [7] can easily be generalized to read:

$$\Delta P_m = \frac{2\sigma}{R_m(z)} + \Delta P_m^0 + \rho_1 g(h_1 - h_1^0) + \rho_2 g(h_2 - h_2^0) - \Delta \rho g(z_t - z) \quad . \quad [11]$$

Since Eq. [8] provides a good approximation of the mean radius at the drop equator, Eq. [11] is applied at $z=z_e$, which requires that the distance between the drop equator and tip, $z_t - z_e$, be known. Figure 8 shows experimental measurements of $z_t - z_e$ during drop growth for four different liquid/gas and liquid/liquid systems, as indicated in the insert. When distance is nondimensionalized by the final drop volume, V_d , raised to the 1/3 power, and the transient drop volume is nondimensionalized by the final volume, data for all systems reduce to a single mastercurve. This correlation is independent of tip size and holds for both pure and surfactant-containing systems. A simple 4th-order polynomial fit of the reduced data shown in Fig. 8 is used to calculate $z_t - z_e$ for subsequent use in Eq. [11].

Materials

n-Dodecane (99+%), 1-octanol (99+%), and 1-decanol (99+%), obtained from Aldrich Chemical Co., Triton X-100, obtained from Baker Chemical Co., and Kodak electrophoresis grade sodium dodecyl sulfate (99+%) were used without further purification. Distilled water, deionized with a four stage Milli-Q™ reagent grade water system from Millipore® with surface tension of 72.5 mN/m, was used in all experiments. In all liquid/liquid measurements the phases were pre-equilibrated for 24 hours prior to an experiment. In all liquid/gas measurements the cell was filled and allowed to equilibrate for at least 2 hours

before measurements were taken. All experiments were undertaken at atmospheric pressure and at 23.0 ± 0.5 °C.

RESULTS

Figure 9 shows results of measurements taken on three surfactant-free systems. This plot combines data for many different drops at different flow rates using different tip sizes. Time ranges over four orders of magnitude with zero time for each drop defined as the time the previous drop detached from the tip. For these surfactant-free systems there should be no measurable dynamics; measured tensions should correspond to the known literature values (34, 35). For the water/air and water/1-octanol interfaces, this is indeed the case. The water/dodecane interface however, exhibits a slow decrease in the tension over time. This decrease is probably due to the presence of small amounts of polar surface active impurities even the highly purified dodecane (35). Our results show that the growing-drop method gives reliable tension measurements in spite of the approximations made in calculating the drop shapes. We also find that the method works well for different tip sizes, for many flow rates, and for both liquid/gas and liquid/liquid systems. Most impressive is the large range of times and tensions spanned by the method.

Figure 10 graphs dynamic tensions for drops of a 0.25 mM aqueous 1-decanol solution growing from a 0.51 mm OD tip into pre-equilibrated air. Two curves obtained by connecting individual maximum-drop-pressure and drop-volume data points are shown along with growing-drop measurements for several different flow rates. At later times all three measurements converge and approach the equilibrium tension of 28 mN/m (36). The growing-drop tensions are measured continuously from the time the drop is hemispherical until the time of detachment, and thus span the interval between the maximum-drop-

pressure and drop-volume points. Very interesting behavior is seen at times less than 10 s. The dynamic tension starts at a low value, initially increases to a maximum, and then decreases to equilibrium. Nonmonotonic behavior is more pronounced at higher flow rates.

The reason for the unique behavior in Fig. 10 is readily understood by considering the relative rates of surfactant depletion due to stretching of the interface, and surfactant replenishment due to transport from the bulk phases to the interface. The rate of area dilatation, $d\ln A/dt$, of a drop growing at constant flow rate can be calculated from Eq. [8]. It starts near zero, approaches a maximum shortly before the drop is hemispherical, and then falls. Figure 11 illustrates the effect that such a non-uniform rate of stretching has on the dynamic tension of a surfactant-laden growing drop. At early times when the rate of dilatation exceeds the rate at which surfactant is transported to the interface, the amount of surfactant at the interface per unit area decreases, and the tension increases. At later times when the rate of dilatation slows, surfactant repopulates the interface, and the tension falls.

Maximum-drop-pressure and drop-volume measurements obtain only one value of tension during drop growth measured as a function of interval time. Hence they give no indication of the nonmonotonic time course of dynamic tension. Interpretation of these "snapshot" measurements requires that the complete transient tension history be inferred from a single data point. Conversely, the growing-drop experiment reveals the entire dynamic tension history. For example, in interpreting dynamic drop-volume surface tension measurements, it is commonly assumed that the interface left behind when a drop breaks off is totally depleted of surfactant (2, 37). If this assumption were correct, growing-drop tensions should start at a value close to the tension of pure water and should decrease monotonically to the final equilibrium tension. Figure

10 clearly contradicts this assertion. The nonmonotonic behavior of the growing-drop tensions in Fig. 10 indicates that a significant amount of surfactant is present on the remnant interface after breakoff. It is the rapid stretching during early drop growth, not the breakoff process, that actually depletes the interface. Any interpretation of dynamic interfacial tension at the surface of growing liquid drops (or growing bubbles) must include consideration of the actual initial state of the interface and the rate of interfacial stretching as well as the mechanisms and rates of transport of surfactant between the bulk and the interface. The interval time drop-volume and maximum-drop (or bubble)-pressure methods cannot uncover these important issues.

Figure 12 graphs dynamic tension data for a liquid/liquid system with surfactant present: drops of 0.02 kg/m^3 aqueous solution of Triton X-100 growing outward into pre-equilibrated n-dodecane. The general behavior is very similar to that seen in the gas/liquid system of Fig. 10, indicating that at early times the rate of stretching exceeds the rate at which surfactant can be supplied to the interface. For this particular liquid/liquid system the density difference between the fluids is relatively small, and the drops grow to larger sizes before detachment. This allows extension of the technique to longer time scales. A problem, however, arises in that with a fixed noise level in the pressure measurement (i.e. 1 Pa) larger drops show more scatter in the tension measurement. This scatter is evident in Fig. 12 at later times. Improvements in vibration control and in filtering of the slowly changing pressure signal at later stages of drop growth should greatly reduce this scatter.

The data in Figs. 10 and 12 are for fairly dilute solutions in which surfactant is transported slowly to the interface. Figure 13 shows data for a system in which the surface tension equilibrates more rapidly. The upper data, for drops of freshly prepared, 6mM SDS solution growing into air, display none of

the nonmonotonic behavior of the earlier two systems. At times less than 1 s only a slight elevation and a monotonic decrease in tension to the equilibrium value occurs. The flow-rate dependence of the SDS dynamic tension is not strong. The small deviations from equilibrium and the hint of a pre-hemispherical maximum in the dynamic tension in Fig. 13, suggests that during the pre-hemisphere growth of the drops, the rate of dilatation only slightly exceeds the rate of surfactant transport, and the rate of dilatation for the entire post-hemisphere period is slower than the rate of surfactant transport.

Data for freshly prepared SDS indicate that the surfactant is very pure. The high value of the equilibrium tension compares well with data for highly purified SDS (22), and the rapid leveling off of the dynamic tension provides a further indication of surfactant purity (22). We then aged the solution for several days and repeated the growing-drop measurement. The lower data in Fig. 13 show results of these measurements. The aged solution exhibits the same initial decrease in tension as the pure surfactant, but the tensions are lower. Then the tension increases to a maximum equal to the fresh solution equilibrium value and finally decreases slowly toward a lower equilibrium tension.

It is well known that SDS hydrolyzes in water to form dodecanol, and that even trace amounts of dodecanol can drastically lower the equilibrium tension and slow down the equilibration time (22, 38). The presence of dilute dodecanol impurity explains the complex time evolution of surface tension in the experiments on the aged SDS solution. Qualitatively, dodecanol should show the same type of behavior in this experiment as the shorter chain length decanol of Fig. 10. In the mixed system of SDS and dodecanol the interface initially contains a mixture of both surfactants. During the pre-hemisphere time period, the rate of dilatation is higher than the adsorption rate of either surfactant, as indicated by the apparent initial maximum. However, the rate of dilatation soon falls below

the transport rate of the SDS, as seen in the pure SDS data, and the tension falls as the SDS approaches its equilibrium adsorption. The dodecanol, however, continues to be depleted until much later times, once the SDS reaches equilibrium coverage, depletion of the impurity dominates. This explains the increase in tension seen beyond 1 s. Finally, when the rate of dilatation decreases further, the dodecanol repopulates the interface, and the tension again diminishes.

DISCUSSION

The data shown above provide just an indication of the utility of the growing-drop technique. The ability to study both liquid/liquid and liquid/gas tensions of both clean and surfactant-containing systems over a large range of time scales makes this a very widely applicable technique. Direct comparison of the growing-drop measurement with the drop-volume and maximum-drop-pressure measurements provides a convenient check on the accuracy of the measurement. Because the approximations used in calculating the tension are most accurate at low Bond numbers, the growing-drop technique is particularly useful for measurements in systems with very small density differences. In studying mixtures of surfactants with widely different transport rates, the growing-drop technique illustrates the dual time scales of the system much more clearly than techniques which can measure only monotonic decreases in tension over time (i.e., interval time measurements).

Another advantage is the ability to examine surfactant adsorption for both rapidly stretching and nearly stationary interfaces within the same experiment. Techniques for measuring nonequilibrium interfacial tension usually divide into two categories; dynamic interfacial tension measurements and surface elastic modulus measurements. The distinction between these two types of measurements is normally made based on the type of disturbance to which the

interface is subjected. Experiments in which an interface is rapidly formed and the tension relaxation of the interface is then monitored in time (time domain experiments) are typically referred to as dynamic interfacial tension measurements. Experiments in which the interface is expanded and contracted periodically and the surface tension is measured as a function of the rate of area change (frequency domain experiments), are typically referred to as surface elastic modulus measurements.

In the growing-drop technique, each individual drop is monitored in the time domain. Changing the flow rate changes the rate of dilatation, so the flow-rate dependence of the measurement gives specific information on the response of the system as a function of dilatation rate. For small deviations from equilibrium, frequency domain and time domain measurements are readily interconvertable (39, 40). In the growing-drop measurement, however, the deviations from equilibrium are large, and the assumptions of the linearized analyses may not hold. Growing drops hold promise as a tool for measuring and relating the surface elastic modulus and the dynamic interfacial tension far from equilibrium.

Many extensions of the growing-drop apparatus are possible. The measurement can easily be run at elevated or lowered temperatures, and with a suitable enclosure at elevated pressures. As long as the flow-rate and wetting behavior of the tip are known, the necessity of directly viewing the growing drops is eliminated. Thus dynamic and equilibrium tensions of opaque fluids can be measured. This makes the growing-drop technique particularly suited for measurements on crude oil systems at actual reservoir conditions. With simple modifications of the fluid delivery system, the same apparatus can be used to study contracting or oscillating interfaces as well as expanding interfaces. This would allow for direct study of surfactant desorption kinetics as well as

adsorption. With slight modification of the cell, the growing drop can be formed pendant up to study liquid/liquid systems in which the less dense fluid is nonwetting.

The demonstrated time scales of the technique (0.05-200s) can readily be expanded. With the ISCO pump used in this work, the lowest possible flow rate is 0.1 mm³/min or a full order of magnitude lower than that used in the experiments discussed here. At such low flow rates, the rate of stretching of the interface already approaches zero. However, if even longer times are desired, the pump can be turned off, and the pressure of the stationary drop can be recorded for as long as desired.

Currently two factors affect the ability to take measurements at very short times. First, short-time measurements correspond to times before the drop reaches a hemispherical shape. Determining accurately the radius of the pre-hemisphere drops is difficult. Further, any small amounts of compressibility in the system lead to a non-constant volumetric growth rate of the drop, and the description Eq. [8] gives of drop radius does not hold. Compressibility is most significant during the pre-hemispherical portion of drop growth. Fortunately, it can be made negligible for the post-hemisphere growth period by careful elimination of all gas bubbles. The need for strictly constant volumetric flow is eliminated if the drop radius can be accurately measured using a video system. Unfortunately, higher speeds and higher resolution are necessary than is possible with standard video equipment.

The second factor affecting the early time measurement is the rate of data acquisition. With the Remote Measurement Systems ADC-1 and our data acquisition software, the fastest possible speed of acquisition is 50 Hz. This limits the shortest time scale to 0.05 seconds. With faster data acquisition time resolution is improved, but the noise level of the signal increases greatly as higher

frequency vibrations of the drop are amplified. Passerone et. al. (30) found that the optimum frequency for sampling to eliminate vibrational noise with growing liquid drops is 20 Hz. A compromise between high rates of data acquisition and noise elimination can be reached by using fast data acquisition at the early times of drop formation when the pressure signal changes rapidly and the signal to noise ratio is large, and a lower rate of data acquisition or data smoothing at later times when the signal changes more slowly and the signal to noise ratio is high.

Signal noise currently limits the tensions which can be measured with this technique. With a noise level of 1 Pa and a tip size of 0.5 mm, the resolution in tension at later stages of drop growth is 1 mN/m. To measure tensions much lower than 10 mN/m, the signal to noise ratio must be improved. Placing the cell on a vibration isolation table will reduce the drop vibrations, but to eliminate vibrations completely the cell must also be mechanically isolated from the liquid supply pump.

Tip design is an area in which substantial improvements are possible. Capillary materials or coatings which make the tip more gas wetting will increase the utility of the growing drop with liquid/gas systems. A quantitative criteria for optimum tip size selection is also needed. To minimize drop elongation, Bond numbers should be low. The magnitude of the pressure signal is also greatest for small radius drops. These considerations argue for small tips. On the other hand, if too small a tip is used, viscous pressure losses dominate the pressure measured by the transducer. Problems of non-constant flow in the drops and tip climbing also become increasingly severe as the tip size decreases. Of the three tips used in this work, the 0.30 mm tip worked best for liquid-liquid systems with tensions of less than 20 mN/m where maximizing the pressure signal was critical. In all systems with tensions higher than 50 mN/m the 0.51 mm tip was necessary to maintain constant flow rate into the drops. In all

liquid/gas surfactant containing systems the 0.51 mm tip helped prevent drops from climbing the tip. A 0.62 mm tip was tested, but drop elongation was too severe for the low Bond number drop profiles to apply.

CONCLUSIONS

The growing-drop technique is a valuable new tool for the study of both liquid/gas and liquid/liquid nonequilibrium interfaces over a wide range of times from ms to greater than hours. Growing-drop measurements on surfactant-free water/air and water/octanol interfaces yield constant values equal to known equilibrium values. For surfactant-laden drops, the growing-drop method follows the actual history of dynamic interfacial tension and also allows concomitant measurement of the maximum-drop-pressure and drop-volume interfacial tensions as a function of drop interval time. Quantitative interpretation of this technique is possible due to the well-defined interfacial stretching rates and radial-growth hydrodynamics (29).

The utility of the growing-drop measurement for understanding interfacial surfactant transport has been explored in three different systems: aqueous 1-decanol/air, aqueous Triton X-100/dodecane, and fresh and aged aqueous SDS/air interfaces. Transport of 1-decanol from a 0.25 mM aqueous solution to the liquid/air interface and transport of Triton X-100 from a 0.02 kg/m³ solution to the water/dodecane interface occur more slowly than the highest rates of dilatation achieved in the growing-drop experiment. This leads to a maximum in the growing-drop dynamic interfacial tension which is not apparent with tension measurements using interval methods. Transport of SDS from a 6 mM aqueous solution to the liquid/gas interface occurs more rapidly than the rates of dilatation achieved in the experiment as is indicated by the monotonic decrease in dynamic surface tension.

The slight amount of dodecanol impurity in aged SDS solutions drastically alter the dynamic surface tension obtained with the growing-drop technique, in that dilute dodecanol transports to the interface much more slowly than the primary component. These two very different time scales of transport are clearly seen in the growing-drop dynamic surface tension measurements, where the initial decrease in tension is followed by a subsequent increase to a maximum tension and finally a decrease in tension to equilibrium.

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NOMENCLATURE

A	= drop area, m^2
Bo	= drop Bond number
D_t	= capillary tip inner diameter, m
f	= tabulated drop-volume correction factor
g	= acceleration due to gravity, m^2/s
h_1^0	= vertical distance between transducer face and dense phase meniscus during "zero" measurement, m
h_2^0	= depth of light phase during "zero" measurement, m
h_1	= vertical distance between transducer and tip faces, m
h_2	= vertical distance between tip face and light phase meniscus, m
ΔP	= pressure drop across an interface, Pa
ΔP_v	= viscous pressure drop between transducer and drop, Pa
ΔP_m^0	= viscous and initial hydrostatic pressure measured by transducer, Pa
ΔP_m	= total pressure measured by transducer, Pa
Q	= flow rate, m^3/s
R_m	= mean radius of curvature of an elongated drop, m
R	= radius of spherical drop, m
R_t	= tip radius from which the drop grows, m
R_1, R_2	= principal radii of curvature of elongated drop, m
Re	= tip Reynolds number
t	= time, s
U	= average velocity of fluid emerging from tip, m/s
V	= drop volume, m^3
V_d	= final drop volume at detachment, m^3
V_o	= hemispherical drop volume, m^3
z	= distance measured from drop apex, m
z_e	= distance from drop apex to drop equator, m
z_t	= distance from drop apex to tip, m

Greek Symbols

θ	= azimuthal angle along drop surface, rad
κ	= surface dilatational viscosity, $Pa \cdot m \cdot s$

μ_1	= inner fluid viscosity, Pa·s
μ_2	= outer fluid viscosity, Pa·s
$\Delta\mu$	= viscosity difference $\mu_1 - \mu_2$, Pa·s
θ	= azimuthal angle along drop surface, rad
ρ_1	= inner fluid density, kg/m ³
ρ_2	= outer fluid density, kg/m ³
$\Delta\rho$	= density difference $\rho_1 - \rho_2$, kg/m ³
σ	= interfacial tension, mN/m

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Figure 1

Figure 2

a

b

c

d

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

t_0

Initial state
after breakup

t_1

Fast stretching and
surface depletion

$$\frac{1}{A} \frac{dA}{dt} > \frac{1}{\tau}$$

$(\sigma \uparrow)$

t_2

Stretching slows and surfactant
adsorbs

$$\frac{1}{A} \frac{dA}{dt} < \frac{1}{\tau}$$

$(\sigma \downarrow)$

Figure 11

Figure 12

Figure 13

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